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Instructions for use

TRACE ELEMENT CONCENTRATIONS OF MANGANESE DEPOSITS IN THE TOKORO BELT, HOKKAIDO, JAPAN

by

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(with 4 text-figures, and 4 tables)

Abstract

  X-ray fluorescence(XRF) analytical methods have been developed to determine Mn, Fe, Cr, Co, Cu, Ni, Zn, Ba, and Pb contents in manganese ores. Standards were prepared from 7 reference samples analyzed by ICP and synthetic samples because the silicate standard samples of GSJ can not be used to analyze the manganese ores. Pellets were prepared by mixing 2.5 g of samples and 3.5 cc polyvinyl alcohol solution, and were subjected to a pressure of 5,000 kg per square cm. Brief geochemical interpretation shows that manganese deposits in the Tokoro Belt have been considered to be formed by submarine hydrothermal activity. Trace elements of the manganese ores are of two distinct types: one type has rather high chemical concentrations such as hydrogenous deposits(deep-sea ferromanganese nodules), the other has low concentrations which is similar to those of submarine hydrothermal deposits. These compositional trends of manganese deposits in the Tokoro Belt is considered as a reflection of a submarine hydrothermal origin with limited hydrogenetic effects on the deposits.

Introduction

  The determination of trace elements in various matrices has been attracting much attention for geochemical application. In order to understand the origin and formational processes of manganese deposits, a large number of analyses are required. This idea suggests that x-ray fluorescence spectrometry is one of the preferred methods because of its high sensitivity for the determination of trace elements and a wide range of analytical elements can be covered by rather simple analytical procedures. The x-ray spectrometry analysis is done by adjusting the effects of radiation enhancement and absorption related to the compositions of standard and unknown samples. The silicate standard samples which were adopted by Ando(1987) for x-ray spectrometry analysis can not be used to analyse the composition of the manganese ores because the effects of absorption and enhancement related to the chemical composition of unknown samples are different from those of standard samples(Calvert et al., 1985).

  The trace elements in manganese deposits are important in understanding the formational processes as was pointed out by Watanabe(1957). Accumulation of the geochemical data of manganese deposits from various present day marine environments and better understanding of their origin make it possible to apply these

data to deducing the origin of terrestrial Mn-deposits. The formational processes of manganese deposits on the land which occur within the chert beds and greenstone are discussed by Bonatti et al. (1976), Crerar et al. (1982), Panagos and Varnavas(1984), Peters(1988), and Varentsov et al. (1988).

Three stratigraphic units, namely the Yubetsu, Saroma, and Nikoro Groups have been recognized within the Tokoro Belt(Sakakibara et al., 1986). The Nikoro Group mainly consists of greenstone, chert, and often includes small amount of limestone(Bamba, 1984 : Tajika and Iwata, 1987). The manganese deposits and the manganiferous iron deposits occur within the Nikoro Group. The former occur in the chert beds, the latter lie between the bedded chert and basaltic pillow lava.

In this paper, we described the calibration lines for Mn, Fe, Ba, Co, Cu, Ni, Pb, and Zn using the synthetic samples and 7 manganese ores which have been analyzed by an inductively coupled plasma emission(ICP) spectrometer. Geochemical interpretation of early Cretaceous manganese deposits in the Tokoro Belt is presented below.

Experiments

All measurements were carried out with a Philips PW 1404 wave length-dispersive sequential automatic spectrometer with an Rh anode tube. The operating condition in this work is given in Table 1. A DEC PDP-11 microcomputer controls the spectrometer. After setting up all factors to measure, unknown samples are determined up to 72 samples each running time using the automatic sample changer.

2.5 g of finely ground ore sample pulverized to 400 mesh in an agate mortar and then mixed with 3.5 cc polyvinyl alcohol solution(Sakai et al., 1987). The mixture was then transferred to 32 mm-diameter aluminum ring. The disc was formed at 5,000 kg/cm² pressure for 5 minutes. These pellet samples were dried out in an air-tight container for 4-5 hours and stored in the dessicator to prevent them from

Table 1 Instrumental condition.

	Ba	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Tube(kV)	50	60	50	60	50	50	50	75	60
(mA)	60	50	60	50	60	60	60	40	50
Collimator	F	F	F	C	F	F	F	F	F
Crystal	1	1	1	1	1	1	1	1	1
Angle(2θ)	87.11	52.81	69.36	49.10	57.54	62.99	48.67	33.92	41.81
Detector	FL	FL	FL	FL	FL	FL	FS	FS	FL
Background slope factor	0.847	0.541	1.252	1.049	2.836		0.556	0.571	0.581

F : fine ; C : coarse 1 : LiF 200, lithium fluoride ; FL ; flow counter ;
FS : flow and scintillation counter. All analysis occurred with Rh-tube and vacuum path

Table 2 The composition of standard samples, values in ppm except Mn and Fe.

	S3	S4	S5	S6	S7	S8	S9	S10
Mn	88.75	96.49	98.14	98.96	99.45	99.72	99.86	99.93
Fe	5.73	1.79	0.947	0.5297	0.266	0.134	0.0675	0.0345
Cr	4603	1435	759	425	238	120	60	30
Co	4956	1544	817	458	256	129	65	33
Cu	4630	1359	719	403	226	114	57	29
Ni	5213	1625	860	482	270	136	69	35
Zn	5075	1582	837	469	263	133	67	34
Pb	5023	1566	828	464	260	131	66	33
Ba	26000	8102	4287	2402	1345	678	342	64

	A1	A2	A3	A4	A5	A6	A7
Mn	42.90	78.40	40.60	57.00	75.10	55.70	9.59
Fe	0.046	0.318	0.207	0.815	0.025	0.045	5.35
Cr	9	15	11	14	11	13	48
Co	3	201	3	31	736	135	48
Cu	69	6290	73	13	1430	84	32
Ni	45	29	43	3	310	378	62
Zn	83	83	97	84	179	189	64
Pb	18	60	6	59	59	34	0
Ba	817	73	2430	6000	441	1040	1040

S3-S10: synthetic standard samples
A1: Nimi A2: Hanaishi A3: Akan A4: Komagadake A5: Yunosawa A6: Nagatoyo A7: Pirika

absorbing moisture because this absorption may give erroneous results.

The synthetic standards were prepared to determine the element concentrations in manganese ores and for the analyses of wide range of trace elements. The standard samples were prepared by mixing MnO_2 and appropriate amounts of trace elements. At first, the mixture containing 10 percent of each trace element was made and then half was separated accurately weighed, mixed with equal amount of MnO_2 and then homogenized in an agate mortar for 30 minutes. This procedure was repeated until the concentrations of trace elements reach several ppm. Table 2 shows the composition of standard samples used in the present study.

Correction

Matrix correction

X-ray emission analysis of trace elements in ores requires to compensate the matrix differences between standard and unknown samples. Matrix effects depend on the grain size of the sample, the orientation of the mineral grains, the absorption or enhancement of the radiation by other elements and the mineral species in which the element is bound.

In most cases, the calibration line deviates from linearity because of the matrix effect. Matrix correction should be applied on the calibration line. In this study the D. J. model(de Jongh, 1973) is used because this model is applicable for the calibration of samples where both absorption and enhancement effects are present. The simplified equation of the de Jongh model was shown by Tsuchiya et al. (1989).

Background and interference correction

The x-ray spectrometry involves the measurement of the fluorescence intensity of a particular element in a sample. In high or moderate concentrations, only the usual measurement is required, but for low concentrations, a background correction should be applied. The slope method, one of the several background methods, was employed in this study. The background profiles were determined by measuring the intensity of the peak and the background position. The background slope factors are shown in Table 1. Ogasawara(1987) described this method in more detail.

Adjacent spectral lines interfere with the peak and background of measurement. In this study it was found out that the iron peak($K\alpha$) interfered with the peak of MnKβ because the manganese concentrations of samples are usually higher than silicate rocks. The effect of MnKβ should be eliminated to get the proper iron Kα intensity. The interference coefficient was calculated using the relationship between the peak count rates obtained from pure reagent and its mixtures with manganese and iron(Norrish and Chappell, 1977).

Analytical Results

The analytical results of the samples are shown in Table 3 with reference val-

**Table 3** Analyses of manganese ores and the reference values analyzed by ICP.

	Nimi	Hana-ishi	Akan	Komaga-dake	Yuno-sawa	Naga-toyo	Pirika
Mn	42.51 (42.90)	78.80 (78.40)	39.90 (40.60)	58.30 (57.00)	74.31 (75.10)	55.90 (55.70)	9.69 (9.59)
Fe	0.038 (0.046)	0.323 (0.318)	0.027 (0.207)	0.764 (0.815)	0.034 (0.025)	0.043 (0.045)	5.37 (5.35)
Cr	7 (9)	29 (15)	11 (11)	16 (14)	3 (11)	12 (13)	12 (48)
Co	1 (3)	360 (201)	6 (3)	68 (31)	714 (736)	68 (135)	28 (48)
Cu	69 (69)	6265 (6290)	75 (73)	9 (13)	1427 (1430)	92 (84)	15 (32)
Ni	40 (45)	20 (29)	36 (43)	7 (3)	298 (310)	380 (378)	62 (62)
Zn	91 (83)	82 (83)	94 (97)	84 (84)	175 (179)	186 (189)	56 (64)
Pb	7 (18)	83 (60)	nd (6)	53 (59)	62 (59)	48 (34)	2 (0)
Ba	63 (64)	828 (817)	82 (73)	2430 (2430)	5968 (6000)	452 (441)	952 (1040)

values in ppm except Mn and Fe ; (   ) reference values.

ues. Text-Figs. 1(a), 1(b), and 1(c) show the calibration lines which were recalculat-
ed by an alpha coefficient of manganese because absorption and enhancement of
manganese affects each elements on x-ray spectrometry analysis.   The calibration
line of copper(Text-Fig. 1(b)) has a slightly high intercept ; which may be due to
tube contamination(Norrish and Chappell, 1977) but the results are rather good.
The analytical results of cobalt were not so good because the CoKα is close to the
manganese absorption edges.   During the analysis, the background was subtracted
automatically.   The high concentration synthetic pellets of Co, Ni, Zn, and Cu
were prepared for high trace element concentration ores such as deep-sea fer-
romanganese nodule samples.   The comparison with the reference data analyzed by
ICP and results by XRF of manganese ores from the Pirika(Table 3) shows good
results, even though the manganese concentration is much lower than others.
These calibration lines may be applied to low manganese concentration samples.
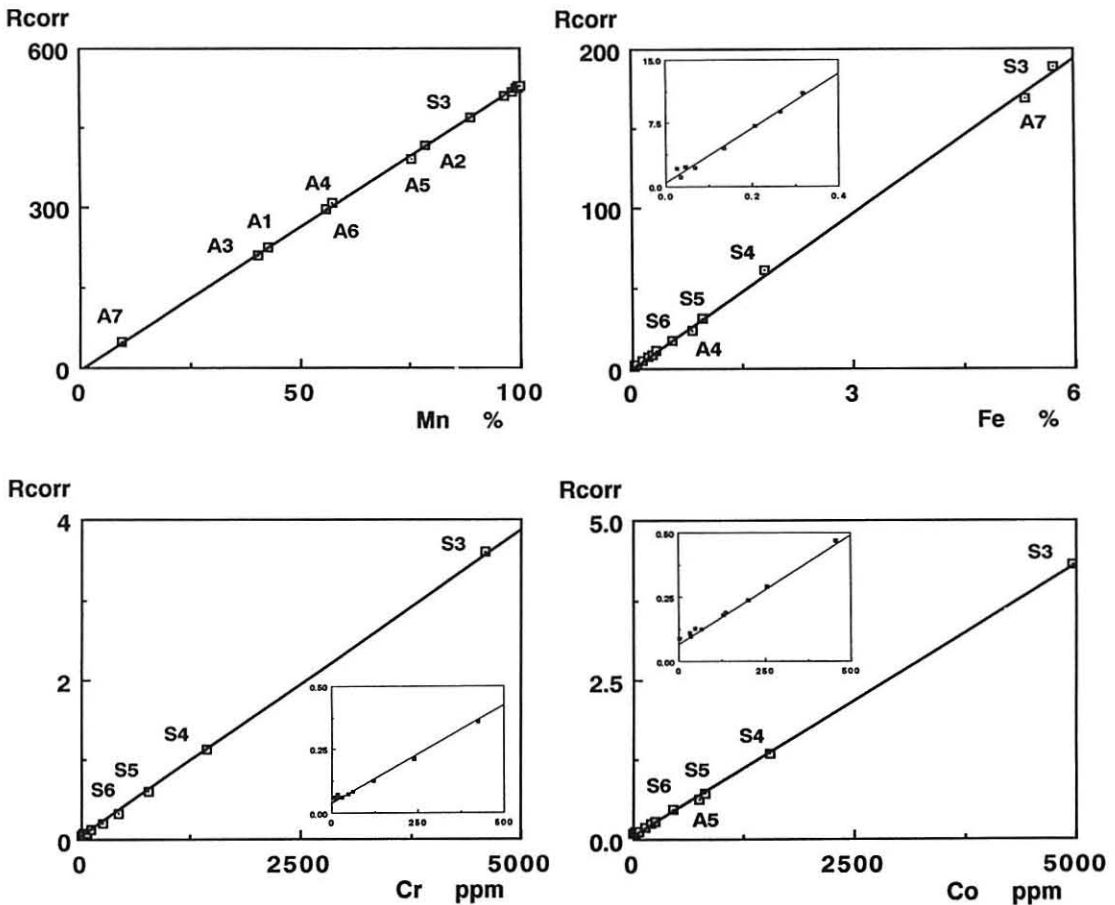
Text-Fig. 1(a) Calibration lines for Mn, Fe, Cr, and Co. Rcorr is the count rates corrected for
matrix effect and line overlap. Cchem: chemical concentration in wt.%. A1: Nimi, A2:
Hanaishi, A3: Akan, A4: Komagadake, A5: Yunosawa, A6: Nagatoyo, A7: Pirika,
S3-S10: syntetic standard samples.
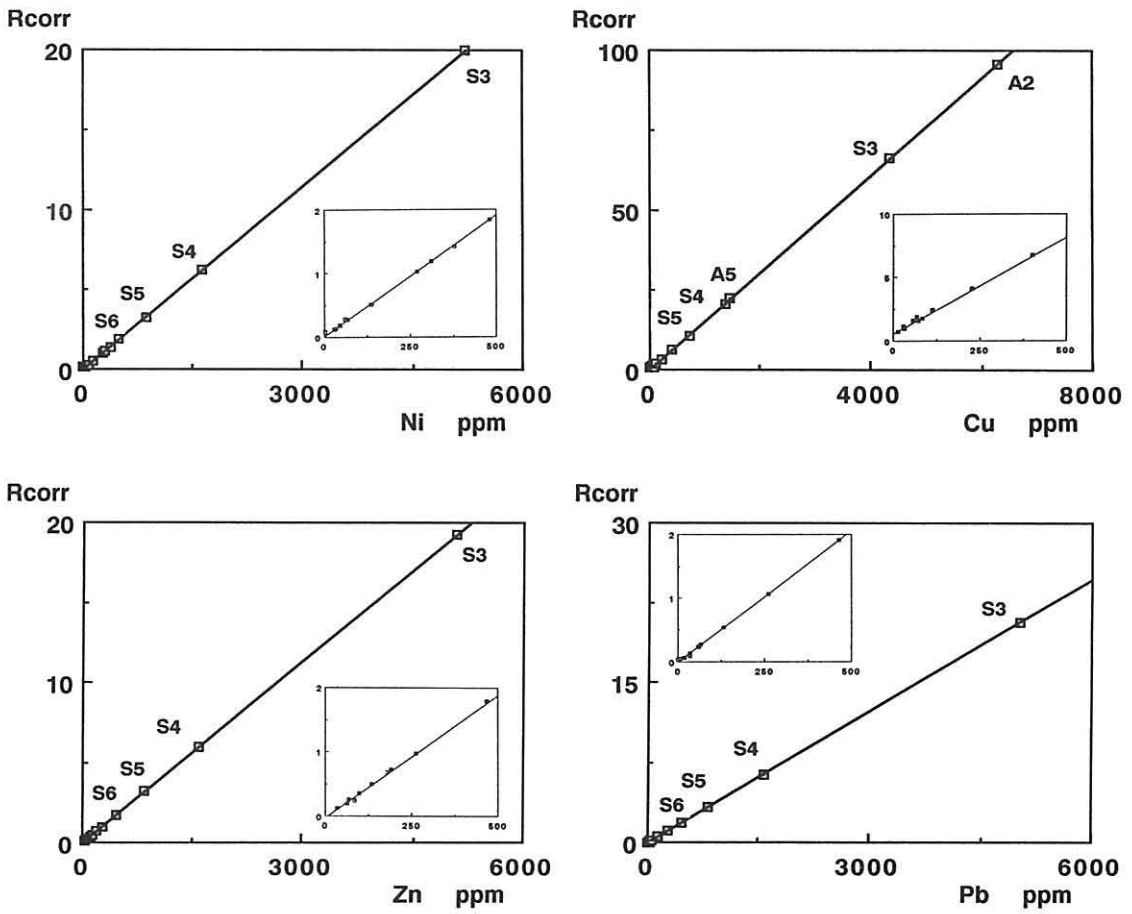
Text-Fig. 1(b) Calibration lines for Ni, Cu, Zn, and Pb. Abbreviations as in Text-Fig. 1(a).
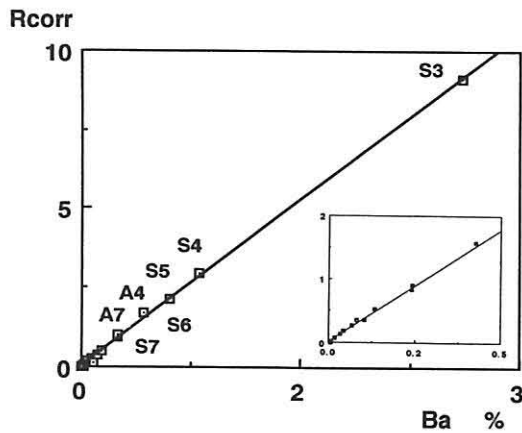
Text-Fig. 1(c) Calibration line for Ba. Abbreviations as in Text-Fig. 1(a).

The comparison with the reference data analyzed by ICP and XRF analysis results should be made with caution because the sample preparation is quite different; the repeated analyses of samples and another pellet from the same area show values differing by less than 10%. Before measuring the unknown samples, the monitor samples were measured. In using monitor samples, drift correction factor to the measurement can be determined using the count rates of the monitored sample.

Geochemical discussion of the manganese deposits in the Tokoro Belt

The manganese oxide deposits of the Tokoro Belt usually occur within the bedded chert(Bamba, 1984). Manganese deposits are conformable, stratiform, and stratabound. The following minerals have been identified in manganese ores from this area : braunite, hollandite, cryptomelane, pyrolusite, todorokite, birnessite, and Mn-pumpellyite.

The analytical results are shown in table 4. The main constituent of the ores is manganese while iron is present in a minor amount. The manganese oxide ores in this study are characterized by low Fe/Mn ratios which is similar to those of submarine hydrothermal deposits. In contrast, the Fe/Mn ratio of the hydrogenous

Table 4 Analyses of manganese ores from the Tokoro Belt, values in ppm except Mn and Fe.

	S1	S2	S3	S4	H1	H2	H3	W1	W2
Mn	66.98	68.43	69.35	69.47	69.35	73.70	73.44	73.81	29.02
Fe	0.15	0.37	0.46	0.65	0.03	0.03	0.03	1.25	0.34
Cr	29	19	22	21	26	22	21	50	7
Co	46	19	10	91	9	2	4	1	1
Cu	1	10	15	12	10	12	20	2	54
Ni	52	45	65	76	56	48	50	26	16
Zn	25	15	20	17	63	29	7	63	26
Pb	8	14	14	8	9	15	15	41	37
Ba	13251	10961	8206	7798	195	144	164	169	2695

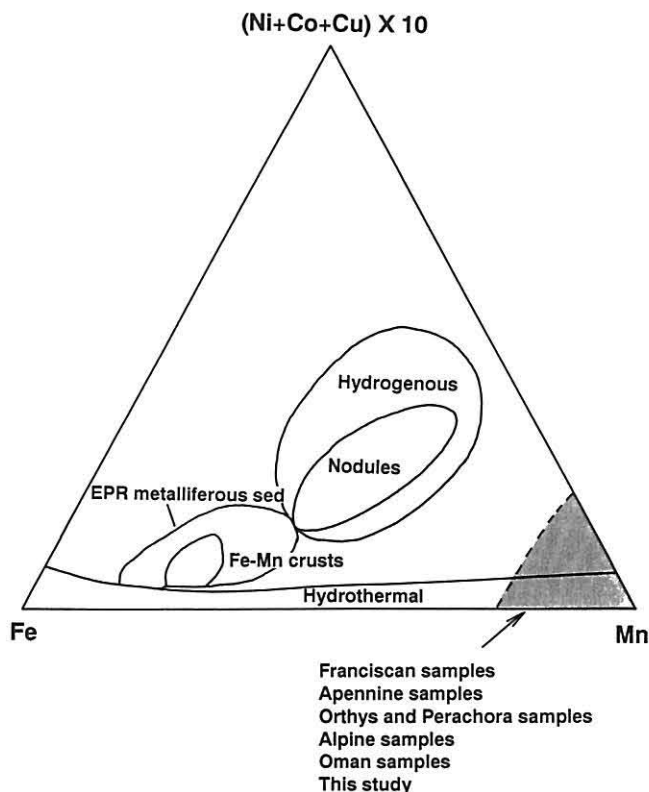|	HN1	HN2	HN3	HN4	K1	K2	K3	M1
Mn	52.50	71.01	69.37	49.41	20.45	41.46	41.44	71.60
Fe	0.35	0.30	0.41	1.36	0.21	0.45	0.45	1.03
Cr	12	19	17	18	10	4	7	13
Co	610	34	22	709	91	132	131	16
Cu	1665	187	220	1665	858	1335	1330	39
Ni	809	103	111	977	237	411	408	41
Zn	330	95	16	409	85	161	141	1
Pb	11	14	29	20	11	15	15	31
Ba	20530	1036	2629	44308	23962	21464	20952	156

S : Syotosibetu mine   H : Hokkaido mine   W : Wakasa mine
HN : Hinode mine   K : Koryu mine   M : Moiwa mine

deposits(deep-sea ferromanganese nodules) is about 1. This means that Fe/Mn ratios of the manganese oxide ores from the Tokoro Belt are similar to those of manganese deposits found near present day submarine hydrothermal center which form by rapid precipitation from hydrothermal solutions. Krauskopf(1957) suggested that a fractionation between these two elements takes place during their formation.

The analytical results of manganese ores in this study generally fall in the hydrothermal area in the Mn-Fe-(Cu+Ni+Co)x10 ternary diagram(Text-Fig. 2). This diagram has been suggested by Bonatti et al. (1972) who attempted a qualitative classification of deep-sea ferromanganese nodules.

Trace element concentrations(Co, Ni, Cu, and Zn) of the manganese ores from the Tokoro Belt are generally lower compared with deep-sea ferromanganese nodules(Table 4). The trace elements of manganese ores in this study have been divided into two types(Text-Fig. 3). One type has rather high chemical concentra-

(Ni+Co+Cu) X 10

Hydrogenous

Nodules

EPR metalliferous sed

Fe-Mn crusts

Hydrothermal

Fe   **Mn**

Franciscan samples
Apennine samples
Orthys and Perachora samples
Alpine samples
Oman samples
This study

Text-Fig. 2 Ternary diagram of Bonatti et al.(1972) with the analyzed samples from the Tokoro Belt and fields of deep-sea manganese nodules and submarine hydrothermal deposits. Also shown are fields of Franciscan samples after Crerar et al.(1982), Apennine samples after Bonatti et al.(1976), Orthys and Perachora samples after Panagos and Varnavas(1984), and Alpine and Oman samples after Peters(1988).

tions such as deep-sea ferromanganese nodules, the other has low chemical concentrations which are similar to those of submarine hydrothermal deposits. Submarine hydrothermal origin Mn-oxide deposits such as the Gulf of Aden, the Famous Area, the Red Sea, and the Galapagos areas generally contain trace elements concentration(Co, Ni, Cu, and Zn) well in excess of normal pelagic sediments but has an order of magnitude lower than hydrogenous ferromanganese deposits (Cronan, 1980). The trace element profiles of manganese ores from the Tokoro Belt were classified into two types even though the ore deposits have been thought to be formed by the submarine hydrothermal origin.
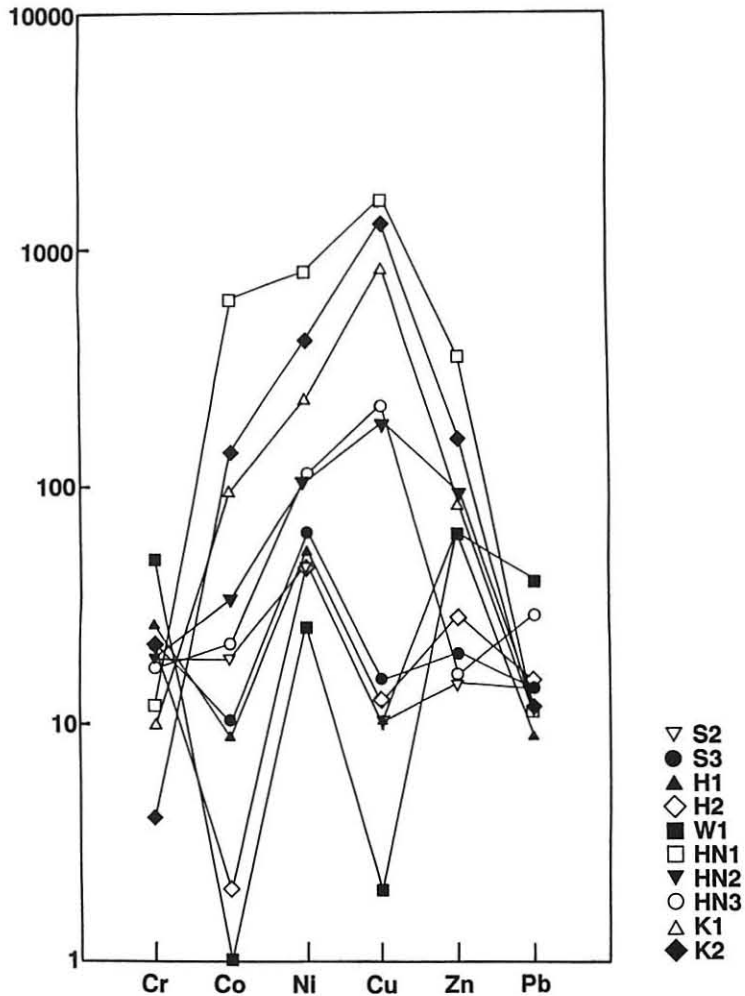
Text-Fig. 3 Representative trace element profiles for manganese ores from the Tokoro Belt. Samples from the Hinode and the Koryu mines have rather higher chemical composition than those of the Syototsibetu, the Hokkaido, and the Wakasa mines. S: Syotosibetu mine H: Hokkaido mine W: Wakasa mine HN: Hinode mine K: Koryu mine

The variable amounts of trace elements are assumed to be a good indication that these elements have different origins. These relationships are indicated in Text-Fig. 4, where the majority of submarine hydrothermal deposits are plotted on the line between Ni and Zn and low concentration of Co. The hydrogenous deposits occupy a field which is relatively high and towards the Co corner of the Zn-Co-Ni triangle. The trace elements Cu, Ni, and Zn are primarily hydrothermal in oringn and Co is predominantly hydrogenous in origin(Crerar et al., 1982). Co has an exceptional crystal field preference for adsorption by tetravalent Mn oxides (Burns, 1976). Plotting the analytical results in this diagram, the chemical concentrations have been separated into two types(Text-Fig. 4). The samples from the Hinode and the Koryu mines were plotted in the hydrogenous origin and those of the Syotosibetu, the Hokkaido, and the Wakasa mines were fallen in the hydrothermal origin area.

The bedded type manganese oxide deposits in the Tokoro Belt seem to belong to the submarine hydrothermal deposits based on the analytical results and geological sequences. According to the trace elements concentrations of manganese ores from the Tokoro Belt, a conclusion can be drawn that the bedded type manganese deposit in the studied area have been mainly formed by submarine hydrothermal activity, and was partly controlled by the process of hydrogenous deposition either at the site of volcanoes or close to it.
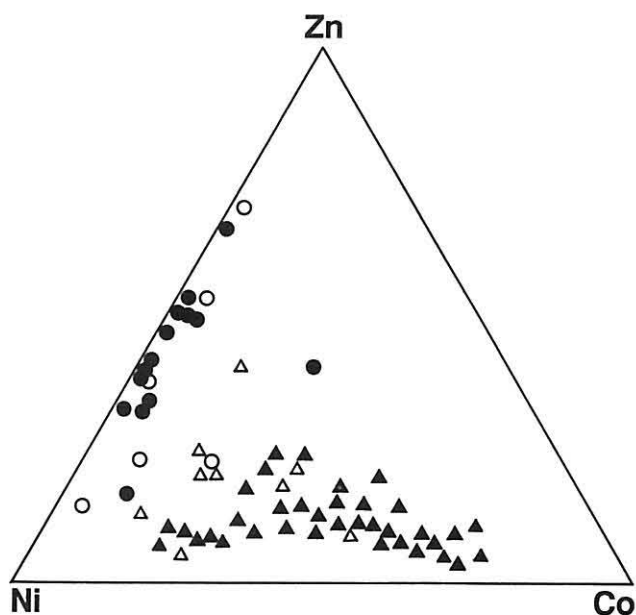
Text-Fig. 4 Zn-Co-Ni diagram. Solid triangles: hydrogenonus deposits(deep-sea manganese nodules) from various environment(after Cronan, 1980): open triangles: ores from the Hinode, the Koryu, and the Moiwa mines; solid circles: submarine hydrothermal deposits (after Cronan, 1980; open circles: ores from the Syotosibetu, the Hokkaido, and the Wakasa mines.

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